Trace analysis of lignin-phenols in speleothems by UHPLC-ESI-HRMS: Comparison of two lignin degradation methods

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1. Motivation
- Speleothems are valuable paleoclimate archives offering the possibility of precise dating up to 600,000 years back.
- Biopolymer lignin as the main constituent of wood in higher plants consists of three monomeric units: sinapyl-, coniferyl-, and coumaryl alcohol.
- Lignin is degraded by alkaline oxidation to its oxidized monomeric units – lignin oxidation products (LOP).
- LOP classified into vanillyl (V), syringyl (S), and cinamyl (C) group.
- LOP composition (S/V and C/V ratio) provides information about type of vegetation e.g. above a cave.

2. Aim of the project
- Adaptation of an alkaline oxidation method to the complex speleothem matrix.
- Replacement of copper(II)-oxide by water-soluble copper-sulfate
- Improved reproducibility and lower detection and quantification limits.
- Lower contaminations and facilitated handling during sample preparation.
- Decreased amount of chemicals and solvents -> Green Chemistry
- Method comparison and application of the proper method to flowstone samples from a cave in the Southern Dolomites.

3. Method
- Flowstone sample
- Dissolve in HCl (conc.) Dilute 1:1 with H2O (Milli-Q)
- CuO degradation: 8 mL NaOH (2 M) 250 mg CuO 50 mg (NH4)2Fe(SO4)3 150°C, 90 min
- CuSO4 degradation: 250 µL NaOH (1 M) 10 µL CuSO4 (10 mM) 10 µL acetic acid (5 L M) 150°C, 90 min
- Add HCl (conc.) + internal standard (ethylvanillin)
- HLB-SPE: 60 mg / 30 mg
- PFP-column (Waters, 2.1x100 mm, 1.7 µm) Flow rate 0.5 mL/min, 40°C
- H2O/ACN gradient

4. Method comparison
- Comparison of LOP-concentration after CuO- and CuSO4 degradation.
- No significant differences among concentration and standard deviation (n=5) observable, therefore the CuSO4 method was applied for further analysis.
- Further evaluation of a GC oven as an alternative to microwave-assisted degradation did not show significant concentration differences.

5. Application
- Analysis of eight timely consecutive samples of a flowstone from a cave in the Southern Dolomites

6. Conclusion and outlook
- Adaptation of a lignin degradation method to speleothem matrix using CuSO4 instead of Cu(II)-O
- Solvent volume decreased from 8 mL to 220 µL with no significant concentration differences.
- Challenging method evaluation due to lack of lignin standards -> high standard deviations among individual LOP concentrations and C/V ratios.
- Application of method to eight timely consecutive flowstone samples: correlations between single LOPs observable -> plotting of S/V to C/V showed characteristic lignin compositions for non-woody angiosperms in all samples.
- Outlook: a) further work to evaluate high standard deviations and optimize sample preparation with the new method
- b) other SPE material, HILIC-MS, analysis of levoglucosan as biomass burning marker in speleothems -> current projects in working group.

References:
2. Schütz, D., Hoffmann, D., (2008), Quaternary Science Journal, 57 (1), 52-76